Surface modification of the TiO_2 particles induced by γ irradiation

LI Zhi* QI Xiangzhi GE Xueping YANG Cunzhong FANG Bin
ZHANG Weidong YANG Xiangmin

Institute of Nuclear Radiation Application, School of Science, East China University of Science and Technology, Shanghai 200237, China

Abstract The surface of anatase TiO_2 was modified by maleic andydride (MAH) γ radiation. The properties of surface modified TiO_2 were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT IR), X-ray photoelectron spectrum (XPS), thermal gravimetric analysis (TGA), as well as transmission electron microscopy (TEM). The results suggest that the MAH anchored on the surface of TiO_2 through chemical bonding and the grafting ratio was approximately 2.7%. TEM image revealed that the modified particles had good dispersibility and compatibility with *N,N*-Dimethylformamide(DMF), which facilitated to hinder the aggregation of TiO_2 particles.

Key words Modification, γ irradiation, TiO_2

1 Introduction

Titanium dioxide (TiO_2) is one of the most important materials for many fields such as catalysts, UV-protective coatings, chemical sensors, solar cells and luminescent devices. But TiO_2 particles are difficult to be dispersed in non-polar solvents stably due to its strong tendency to agglomerate, and have weak combination with the polymer matrix because of poor interfacial interaction. Surface modification of TiO_2, such as coupling agent, sol-gel blending technique, in situ polymerization process, and polymer grafting from the surface of inorganic particles, is considered as the effective way to improve its dispersion in a solvent or a polymer matrix. Among them, graft polymerization of polymer onto the surface of TiO_2 particles has made considerable progress. Obviously, the methods of indirect graft polymerizations are relatively fussy, and easily introduce low molecular weight compounds. Ionizing radiation is a direct, effective, attractive method for contacting inorganic/organic materials interface and modifying surfaces of inorganic materials. many research have focused on changes of physical properties and photo-catalystic effect of modified TiO_2 by laser，UV-Vis light, Electron Beam, γ radiation method. In recent years, X.T. Zu[1,2] and coworkers carried out modification of TiO_2 with methyl methacrylate (MMA) induced by Electron beam radiation and ^{60}Co γ irradiation. Xiuyuan Ni[3] *et al.* investigated the PMMA grafting onto TiO_2 under the UV irradiation. Shaofeng Zhong[4] studied "graft from" polymerization of MMA by N_2 plasma. But researches about grafting monomers onto TiO_2 with direct radiation are relatively few. Although some mechanisms of graft polymerizations induced by ionizing irradiation are still obscure, many researches apply the free radical theory for interpretations. The oxygen on anatase TiO_2 surfaces can initiate the graft polymerization during the radiation. The radiation produced δ anion free radicals on the TiO_2 nanoparticle surfaces with high activation[3]. These radicals can only change the surface properties of the materials rather than the bulk properties[4].

In this article, we reported the surface modification of anatase TiO_2 with MAH through γ radiation. The surface modified TiO_2 were investigated by FT IR, XRD, XPS, TGA, and TEM.

2 Experimental

2.1 Chemicals

* Corresponding author. *E-mail address*: lizhi@ecust.edu.cn

Received date: 2012-12-31

Titanium Dioxide (TiO_2) powder, which was obtained from Sinophsrm chemical reagent Co. Ltd (China), was used without any pretreatment. Maleic anhydride (MAH), Xylene, *N*,*N*-Dimethylformamide (DMF) were all purchased from Shanghai Chemical Works "Ling-feng", China. Other reagents were of analytical grade and used without further purification.

2.2 Modification of the TiO_2 particles induced by γ irradiation

In a glass shallow container, 4.0 g MAH was dissolved in 16.0 g Xylene solution under 80ºC. Then 2.0 g TiO_2 powder was dispersed in above mixture, followed by ultrasonic for 30 min. The container was degassed, and then filled with dry nitrogen at room temperature. The samples were irradiated of 60 kGy doses from a ^{60}Co source at ambient temperature.

After irradiation, the resulted suspension was separated by centrifugation at 3500 rpm for 5 min. the obtained powder was re-dispersed in excessive xylene and centrifuged again. The cycle of "dispersion-centrifugation" was repeated at least 5 times to completely remove the un-reacted MAH on the surface of TiO_2 particles. The samples, g-TiO_2, were dried in vacuum at 70ºC for 12 h.

2.3 Materials characterization

X-ray diffraction (XRD) experiments were conducted to an X-ray diffractometer (RIGAKU, D/max 2550VB /P, Japan) equipped with a graphite monochromator and Cu Ka radiation. The generator was operated at 40 kV and 100 mA. The samples were scanned at diffraction angle from 10–80^o at the rate of 0.02^o/s.

The X-ray photoelectron spectroscopy (XPS) experiments were carried out in ultrahigh vaccum using a spectrometer (PHI 5000C, ESCAC, Japan) using Mg *K*α radiation at 14.0 kV and 25 mA.

Fourier transform infrared (FTIR) spectra was carried out on spectrometer (Nicolet-550, USA) with scanning range of 400–4000 cm^{-1} under ambient conditions using KBr pellets.

Thermal gravimetric analysis (TGA) was determined by a thermalanalyzer (Perkinelmer Inc). Samples were heated from room temperature to 700ºC at the speed of 10ºC/min under air atmosphere.

The morphology analysis was performed on transmission electron micrograph (TEM) analyzer (JEM-2100F, Japan). The TEM specimens were prepared by dispersing the g-TiO_2 particles in absolute DMF by ultrasonic for 30 min and then depositing a small droplet of onto a copper grid covered with carbon film and evaporating the solvent completely at room temperature.

3 Results and discussion

3.1 Modification of the TiO_2 (g-TiO_2)

As shown in Fig.1 TiO_2 possessed peaks at 2θ=25.4º, 37.8º, 48.2º, 55.2º, 62.8º, corresponding to anatase crystalline form[5]. After reaction with MAH, these peaks still remained and intensity unchanged, but the new signal appeared at 28.1º, which should correspond to the MAH. In other words, there was no obvious change in the XRD patterns after radiation induced modification, indicating the modification did not affect the crystalline structure of TiO_2 significantly and the segment of MAH had not entered the crystal pattern of the titanium dioxide. The grafted MAH chains only covered the surface of the titanium dioxide powder. The results were similar to references[4,6].

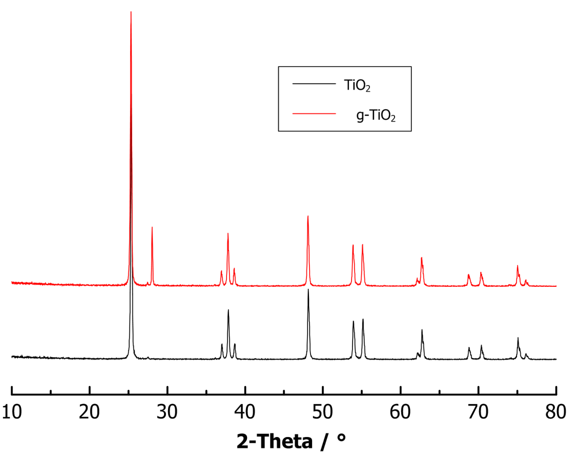

Fig.1 XRD powder patterns of bare TiO_2 and g-TiO_2.

The FTIR spectra of bare TiO_2 and after grafting with MAH were shown in Fig.2. The bare TiO_2 showed a broad band between 3500 cm^{-1} and 3000 cm^{-1}, which indicated the presence of -OH groups on the surface of the titania. A weak band at approximately 1630 cm^{-1} was attributed to adsorbed

water on the TiO_2. The infrared absorption bands between 400 cm^{-1} and 800 cm^{-1} should be assigned to the vibrations of Ti-O and Ti-O-Ti framework bonds[7]. After surface grafting modification, new absorption bands appeared at 1706 cm^{-1}, 1636 cm^{-1} (C=O stretching vibration mode) and 1300–1200 cm^{-1} (C-O stretching vibration mode)[8], which could be originated by the polymerization of MAH onto the surface of TiO_2 particles. Moreover, it could be found that the peak of modified TiO_2 particles at 400–800cm^{-1} shifted to higher wavenumbers. But -OH absorption bands remained slightly after grafting modification. This indicated that the surface group of TiO_2 had changed mostly from Ti-OH to Ti-O-C.

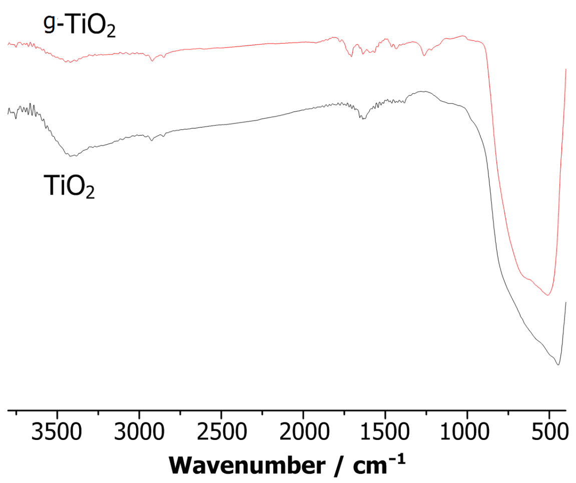

Fig.2 FT IR spectra of bare TiO_2 and surface modified TiO_2 particles.

Further characterization on the surface-modified TiO_2 was conducted by XPS analysis. Fig.3 presented the XPS spectra of modified TiO_2 in the C 1*s* region and O 1*s* region. The C 1*s* peaks at 284.86 eV was probably associated with the adsorption of carbon dioxide (CO_2) on the surface of TiO_2 or a trace amount of hydrocarbon contaminants when air exposed samples were introduced into XPS chambers. Other two peak components at about 285.56 eV and 288.89 eV were assigned to the carbon adjacent to an anhydride (C-C-O(=O)), and anhydride groups (O=C-O-C=O) of MAH units. The O1*s* region was decomposed into five contributions. The peaks at 530.0 eV and 530.7 eV corresponded to Ti-O and the hydroxyl groups (-OH) in TiO_2, respectively. The peak at binding energy of 532.2 eV corresponded to the oxygen species (Ti-O-C), which showed that MAH was grafted onto the surface of the titanium dioxide powder successfully[4]. The peak at 531.7 6 eV arised from the carbonyl oxygen(C=O) of the maleic anhydride unit, whereas the peak at 532.70 eV arised from the ether oxygen C-O-C. Other C 1*s* and O 1*s* peak-fitting results were according to Beamson[9].

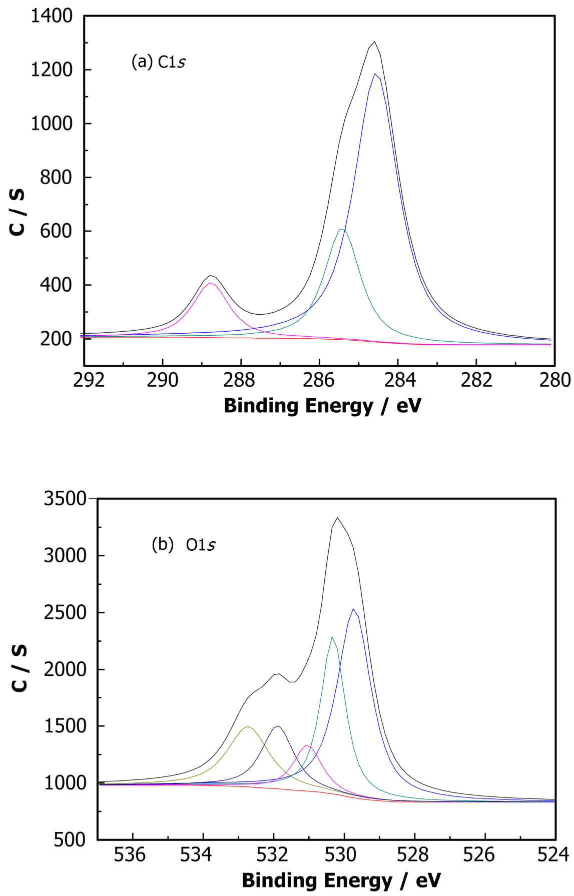

Fig.3 High-resolution XPS spectra of modified TiO_2 in the C 1s (a) and O 1s (b).

Thermal stability of TiO_2 and modified TiO_2 was measured by dynamic thermo gravimetric analysis (TGA) as shown in Fig.4. The thermal decomposition of native TiO_2 began at about 40ºC and the continuous mass loss could be seen from 40ºC to 800ºC. It was found that not-grafted TiO_2 displayed nearly 1.7% weight loss below 800ºC, which was attributed to water absorbed by TiO_2. It could be seen clearly that the decomposition range of grafted TiO_2 was divided into three stages. Weight loss from 40ºC to 120ºC could be attributed to the loss of physically adsorbed water on surface of TiO_2. Weight loss from 120ºC to

150ºC was resulted from the degradation of MAH chains. While the weight loss from 150ºC to 800ºC was resulted from removal of chemically bound water (hydroxyl groups) from the powder surface[10](Fig.4).

TGA was also used to determine the amount of grafted organic materials. The amounts of surface-grafted MAH on the TiO_2 particles were calculated as follows[11].

Grafting ratio=Weight loss%(g-TiO_2)-*Weight loss*% (TiO_2)

It was concluded that 2.65% of MAH were grafted onto TiO_2 particles under γ irradiation. According to the results of TGA, FTIR and XPS, MAH was grafted onto TiO_2 surface successfully with the low grafting ratio. One possible reason was due to low polymerization ability of MAH, which might form a monolayer of MAH onto TiO_2 by irradiation method.

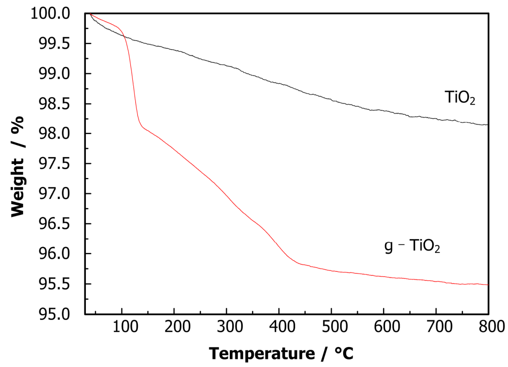

Fig.4 TGA decomposition profiles for TiO_2 and g-TiO_2.

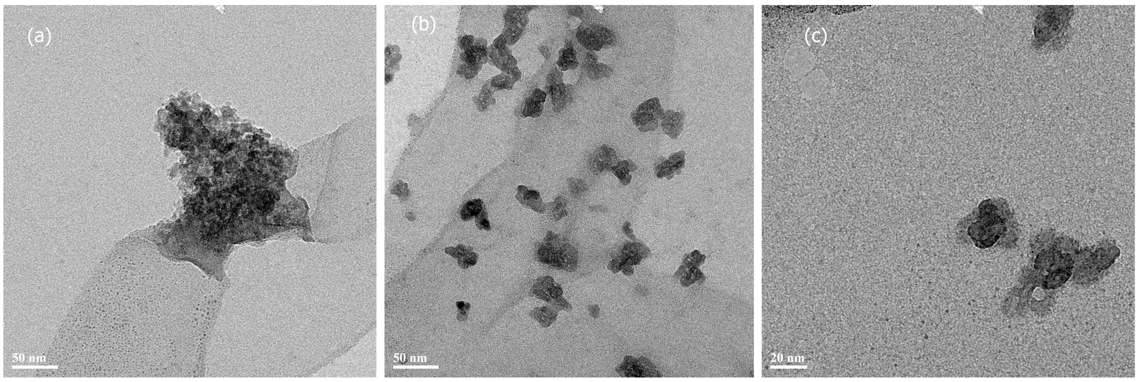

Fig.5 TEM images for TiO_2: (a) untreated particles, (b) and (c) modified with MAH.

Transmission electron microscopy images of TiO_2 and modified TiO_2 dispersed in DMF were shown in Fig.5, respectively. In prepared samples, small size TiO_2 particles existed in the upper layer. The obvious agglomeration could be seen in the images of untreated TiO_2, while the homogeneous dispersion could be seen in the images of modified TiO2 and the agglomerations had been reduced. From Fig.5(c), MAH layers coated on the surface of TiO_2 particles were clearly shown as the gray area. This suggested that MAH introduced onto the surface of TiO_2 not only provided functional groups anchoring TiO_2, but also made the particles disperse in organic solvents compatibly. The molecular chains grafted on the surface of TiO_2 bring mutual exclusion and steric hindrance effect, also the surface free energy had been reduced and the agglomeration controlled[8].

4 Conclusion

MAH coated TiO_2 was fabricated by surface modification method of γ radiation. It was concluded that MAH was covalently linked to the surface of TiO_2 by the surface. Thermogravimetric analysis suggested that the grafting ratio was 2.65. Compared to the origina TiO_2, the grafted TiO_2 had better compatibility and homogeneously dispersion with DMF.

References

1 Wang Z G, Zu X T, Yu H J, *et al.* Nucl Inst Meth Phys Res B, 2006, **250:**196–200.

2 Jiang Bo, Zu X T, Tang F Y, *et al.* J Appl Polym Sci, 2006, **100:** 3510–3518.

3 Ni X, Ye J, Dong C. J Photochem Photobiol A: Chem, 2006, **181:** 19-27.

4 Zhong S F, Meng Y D, Qu Q R, *et al.* J Appl Polym Sci, 2005, **97:** 2112–2117.

5 Chen J H, Dai C A, Chen H J, *et al.* J C Interface Sci, 2007, **308:** 81–92.

6 Wang Z G, Zu X T, Zhu S, *et al.* Phys Lett A. 2006, **350:** 252–257.

7 LuoY B, Wang H L, Xu D Y, *et al.* Appl Surface Sci, 2009, **255:** 6795–6801.

8 Tai Y, Qian J, Zhang Y, *et al.* Chem Eng J, 2008, **41:** 354–361.

9 Beamson G, Briggs, D. High resolution XPS of organic polymer: The Scienta ESCA300 Database; Wiley: Chichester, UK, 1992.

10 Heng Z, Chen H. Appl Surface Sci, 2010, **256:** 1992–1995.

11 Lu X, Lv X, Sun Z, *et al.* European Polym J, 2008, **44:** 2476–2481.